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(54) **Organic-inorganic hybrid polymer material and process for preparing the same**

(57) According to the present application, the characteristics of an inorganic material are suitably supplied to an organic material, and the characteristics of an organic material are suitably supplied to an inorganic material. The organic-inorganic hybrid polymer is obtained by the process in which a polymer having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group, is hydrolyzed and polycondensed to form crosslinkages. Another process is that in which a polymer having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group, and a metal alkoxide compound are cohydrolized and copolycondensed to form crosslinkages.

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Description

[0001] The present invention relates to a polymer material which is useful for various kinds of plastic materials, resin additives, and coating materials.

5 [0002] Various inorganic materials are now widely employed for industrial use in consideration of both property of the material and requirement of the use. A silicic ceramic material, for example, is excellent in mechanical strength, chemical resistance, and thermal stability. A silicic material such as silicone oxide, and titanium oxide additionally has excellent optical properties.

10 [0003] Since the inorganic material is hard and brittle, it is generally difficult to mold and to process the inorganic material. The inorganic material is also poor in adhesiveness with an organic material, and therefore the use is restricted.

[0004] On the other hand, the organic polymer is flexible and is easily processed. However, their hardness and thermal stability are largely inferior to those of the inorganic material.

[0005] Therefore, there is great demand for the material which is able to complement to each other in their properties, and is able to make the use of the respective advantages thereof.

15 [0006] In respect of the problem, for improving physical properties of a plastic material such as surface hardness, gloss, soil resistance, hardness, heat resistance, weather resistance, and chemical resistance, studies of organic-inorganic hybrid polymer material has been made in which an inorganic element such as Si, Ti, and Zr is incorporated.

20 [0007] In the process for preparing the organic-inorganic hybrid polymer material, it is known that an organic monomer or an organic polymer, and an inorganic frame containing compound such as alkylsiloxane are radically copolymerized, or an inorganic functional group such as alkoxy silane is bound to an organic polymer as a pendent group, and then the organic polymer is crosslinked.

[0008] Japanese Patent Kokai Publication No. 57642/1988, 103486/1991, and J. Appl. Polym. Sci., vol. 35, pages 20 to 39, 1988, for example disclose the process for preparing an organic-inorganic hybrid polymer material in which an organic monomer or an organic polymer is radically polymerized by using an alkyl siloxane-containing compound as an initiator. However, it is even difficult to introduce an alkyl siloxane moiety to the both end of the organic monomer or the organic polymer, and it is impossible to introduce a siloxane frame uniformly into the structure of the resulting polymer, by the abovedescribed process in which an alkyl siloxane-containing compound is used as an initiator. At present, the synthesis of the alkyl siloxane-containing compound also requires complicated procedures.

30 [0009] Macromolecules, vol. 24, No. 6, page 1431, 1991, describes the method for preparing a siloxane-containing polymer by the anionic polymerization method. However, in order to obtain the intended polymer material, the reaction conditions must be carefully controlled because the reactivity and the physical property of the employed material are different from each other.

35 [0010] Additionally, the anionic polymerization is high in cost, and it is not practical to conduct the above described process under the industrial scale.

[0011] Japanese Patent Kokai Publication No. 43679/1993, and 86188/1993 describe the process for preparing an organic-inorganic hybrid polymer material in which a vinyl polymer and a silicone compound having a silane group (Si-H group) are subjected to the hydrosilylation reaction, and then the resultant are crosslinked by the sol-gel method.

40 [0012] Japanese Patent Kokai Publication No. 104710/1996, and 104711/1996 describe the process for preparing an organic-inorganic hybrid polymer material in which a vinyl monomer is radically polymerized using an alkoxysilyl group-end capped azoic initiator, and the resulting alkoxysilyl group-end capped vinyl polymer is hydrolyzed and polycondensed. There is described here polystyrene, polyvinyl chloride, an acrylic resin as the vinyl polymer.

[0013] The vinyl polymers however are poor in heat resistance and mechanical strength, and are not suitable for employing as a high-performance plastic material, particularly as a structural material and a hard coating material.

45 [0014] Macromolecules, vol. 25, page 4309, 1992, discloses the process for preparing an organic-inorganic hybrid polymer material in which an alkoxysilyl group is bonded to a main chain of a polyalkylene oxide polymer, and the resultant is hydrolyzed and polycondensed. As the main chain of the organic-inorganic hybrid polymer material, Macromol. Chem. Macromol. Symp., vol. 42/43, page 303, 1991, discloses a polyoxazoline polymer, J. Inorg. Organomet. Polym., vol. 5, page 4, 1995, discloses a polyamine polymer, and J. Appl. Polym. Sci., vol. 58, page 1263, 1995, discloses a cellulose polymer.

50 [0015] However, all the polymers described above as the main chain of the organic-inorganic hybrid polymer material, are hydrophilic. The hydrophilic polymers are hygroscopic, poor in water resistance, and are not suitable for employing as a plastic molded material, a sealing material, a coating raw material, a structural material, a hard coating material, and the like.

55 [0016] On the other hand, hydrophobic polymers, particularly engineering plastics are excellent in heat resistance, mechanical strength, and water resistance. Hydrophobic polymers are widely demanded and employed as an industrial plastic material. The development of an organic-inorganic hybrid polymer material using a hydrophobic polymer is therefore generally required.

[0017] However, hybridization by using a hydrophobic polymer is generally difficult because a hydrophobic polymer is not soluble or hardly soluble into an alcoholic solvent which is usually employed as a solvent for the sol-gel reaction, and the number of reactive functional group in a hydrophobic polymer is generally poor. Therefore, there is no reference which describes the organic-inorganic hybrid polymer material using the hydrophobic polymer.

5 [0018] The hydrophobic polymer generally has a small number of functional group therein as described above. The hydrophobic polymer often has only two functional groups at the terminal ends. As a result, the content of an inorganic moiety of the resulting organic-inorganic hybrid polymer material is up to few % by weight. Such a minor content of the inorganic moiety is not sufficient to improve physical strength of the organic-inorganic hybrid polymer material such as heat resistance, hardness, and the like.

10 [0019] In the process of the sol-gel method, a porous gel is formed by subjecting a raw material such as metal alkoxide to hydrolysis and polycondensation. The porous gel has recently been employed as a catalyst. It is otherwise used as glass or ceramics after that the pores thereof is stopped by sintering at high temperature (e.g., Sumio SAKUKA et al., "Science of sol-gel method").

[0020] Glass is well-known as a material having excellent gas-barrier ability, and is commonly used as a container for sealing. However, the glass has a drawback of heavy and easy to break.

15 [0021] On the other hand, polycarbonate is a material which has relatively poor gas-barrier ability among the engineering plastics. Therefore, the polycarbonate heretofore has not been commonly used as a container for sealing even though it has excellent impact resistance and transparency.

[0022] That is, if the glass and the polycarbonate are combined and the drawbacks thereof are complemented and the advantages thereof are exploited, the resulting material will have excellent properties, and it must be used as an alternate of a glass container or a glass material.

20 [0023] According to the present invention, the organic-inorganic hybrid polymer materials are provided, which have both the characteristics of an inorganic material such as heat resistance, weather resistance, surface hardness, rigidity, water resistance, chemical resistance, pollution resistance, mechanical strength, flame resistance, and the like, and the characteristics of an organic material such as impact resistance, softness, easy-processing, and the like.

25 [0024] By first, the present invention provides an organic-inorganic hybrid polymer material obtained by the process in which a polymer having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group, is hydrolyzed and polycondensed to form crosslinkages.

[0025] The first preferred aspect of the present invention is the process for preparing an organic-inorganic hybrid polymer material in which polymer (A) having at least one functional group in the molecule and a polycarbonate and/or a polyarylate moiety as a main frame, and metal alkoxide (B) having a functional group which may react with the functional group of polymer (A), are reacted to obtain polymer (C) having a metal alkoxide group as a functional group in the molecule, then the resulting polymer (C) is hydrolyzed and polycondensed to form an organic-inorganic hybrid polymer material having three-dimensional cross linkages by the sol-gel method.

30 [0026] According to the first aspect of the present invention, an organic-inorganic hybrid polymer material using a hydrophobic polymer is prepared. The organic-inorganic hybrid polymer material is excellent in heat resistance, mechanical strength, and water resistance. The organic-inorganic hybrid polymer material is therefore preferred to be employed as an industrial material, particularly a plastic molded material, a plastic film material, a sealing material, a raw material for adhesive or coating, a structural material, an optical material, a polymeric silane coupling agent, a resin additive, a surface modifying agent, a hard coating material, and the like.

35 [0027] Secondary, the present invention provides an organic-inorganic hybrid polymer material obtained by the process in which a polymer having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group, and a metal alkoxide compound are cohydrolyzed and copolycondensed to form crosslinkages.

40 [0028] The second preferred aspect of the present invention is the process for preparing an organic-inorganic hybrid polymer material in which polymer (C) having at least one metal alkoxide group in the molecule and a polycarbonate and/or a polyarylate moiety as a main frame, and metal alkoxide (B) are mixed and dispersed finely and uniformly, and the mixture is hydrolyzed and polycondensed to form an organic-inorganic hybrid polymer material having three-dimensional crosslinkages by the sol-gel method.

45 [0029] According to the second aspect of the present invention, an organic-inorganic hybrid polymer material having a hydrophobic polymer as a main frame and an enlarged inorganic moiety content, is prepared. The organic-inorganic hybrid polymer material is particularly excellent in heat resistance, mechanical strength, surface hardness, gas-barrier ability, water resistance, and transparency. The organic-inorganic hybrid polymer material is therefore preferred to be employed as a high performance and a high functional plastic material.

55 Fig. 1 shows a ^1H -NMR spectrum of the alkoxy-silylated polycarbonate prepared in Example 1.

Fig. 2 shows a characteristic curve obtained by the dynamic mechanical analysis of the PCS film prepared in Example 14.

Fig. 3 shows a characteristic curve obtained by the dynamic mechanical analysis of the polycarbonate film prepared in Comparative Example 1.

Fig. 4 shows a SEM photograph of the sol-gel material having PC/TEOS = 3/7 prepared in Comparative Example 11.

Fig. 5 shows a SEM photograph of the silica/PCS material having PCS/TEOS = 3/7 prepared in Example 17.

Fig. 6 shows a characteristic curve obtained by the dynamic mechanical analysis of the silica/PCS film having PCS/TMOS = 7/3 prepared in Example 16.

Polymer (A)

[0030] Polymer (A) of the present invention is the polymer which has at least one functional group in the molecule and has a polycarbonate and/or a polyarylate moiety as a main frame. Preferred examples of polymer (A) include polycarbonate, polyester carbonate, and polyarylate, and the like.

[0031] Polymer (A) may be a homopolymer or a copolymer of plural monomers. Polymer (A) may be a mixture of plural polymers, and it may be linear or branched. Polymer (A) is preferably soluble in a solvent such as hydrocarbon, halogenated hydrocarbon, and ether, and has a number average molecular weight of from 500 to 50000, more preferably 1000 to 10000.

[0032] Polymer (A) have to have at least one, preferably not less than two functional groups in the molecule. The functional group have to be able to react with a functional group of metal alkoxide (B), but a class of them is not particularly limited.

[0033] Specific examples of the functional group include a hydroxyl group, an amino group, a carboxyl group, a thiol group, an alkenyl group, an alkynyl group, an acid halide group, an acid ester group, a formyl group, a halogen atom, an epoxy group, and an isocyanato group. Preferred are those having an active hydrogen atom, such as a hydroxyl group, an amino group, and a carboxyl group. The functional group equivalent weight of the polymer (A) is generally 1 to 50, preferably 2 to 10.

Metal alkoxide (B)

[0034] Metal alkoxide (B) of the present invention is not limited to, and any class of them may be used. Examples of metal alkoxide (B) preferably to be used in the present invention are those represented by the formula (1):



wherein A represents an alkoxy group having 1 to 8, preferably 1 to 4 carbon atoms;

M represents a metal element selected from the group consisting of Si, Ti, Zr, Fe, Cu, Sn, B, Al, Ge, Ce, Ta, and W, preferably the group consisting of Si, Ti, and Zr; and

p represents an integer of 2 to 6.

[0035] Specific examples of metal alkoxide (B) include tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, and tetrabutoxysilane;

titanium tetra-alkoxides such as titanium tetra-n-propoxide, titanium tetra-iso-propoxide, and titanium tetrabutoxide; zirconium tetra-alkoxides such as zirconium tetra-n-propoxide, zirconium tetra-iso-propoxide, and zirconium tetrabutoxide; and

metal alkoxides such as copper dimethoxide, barium diethoxide, boron trimethoxide, gallium triethoxide, aluminium tributoxide, germanium tetraethoxide, lead tetrabutoxide, tantalum penta-n-propoxide, and tungsten hexaethoxide.

[0036] Particularly preferred metal alkoxide (B) to be used in the present invention is those represented by the formula (1) in which M represents Si because silicone alkoxide is easy to apply for general purpose.

[0037] The other examples of metal alkoxide (B) are those represented by the formula (2):



wherein R represents a phenyl group or an alkyl group having 1 to 8, preferably 1 to 4 carbon atoms,

A represents an alkoxy group having 1 to 8, preferably 1 to 4 carbon atoms,

M represents a metal element selected from the group consisting of Si, Ti, Zr, Fe, Cu, Sn, B, Al, Ge, Ce, Ta, and W, preferably the group consisting of Si, Ti, and Zr,

R' represents an alkylene group or an alkylidene group having 1 to 4, preferably 2 to 4 carbon atoms,

X represents a functional group selected from the group consisting of an isocyanato group, an epoxy group, a carboxyl group, an acid halide group, an acid anhydride group, an amino group, a thiol group, a vinyl group, a methacryl group, and a halogen atom, and

k represents an integer of 0 to 5, l represents an integer of 1 to 5, m represents 0 or 1, n represents an integer of 0 to 5.

[0038] Specific examples of metal alkoxide (B) of which metal is silicone, include (alkyl)alkoxysilanes such as trimethoxysilane, triethoxysilane, tri-n-propoxysilane, dimethoxysilane, diethoxysilane, di-iso-propoxysilane, monomethoxysilane, monoethoxysilane, monobutoxysilane, methyltrimethoxysilane, ethyldimethoxysilane, ethyldiethoxysilane, dimethylmethoxysilane, di-iso-propylisopropoxysilane, methyltrimethoxysilane, ethyltriethoxysilane, n-propyltri-n-propoxysilane, butyltributoxysilane, dimethyldimethoxysilane, diethyldiethoxysilane, di-iso-propyldi-iso-propoxysilane, dibutyldibutoxysilane, trimethylmethoxysilane, triethylethoxysilane, tri-n-propyl-n-propoxysilane, tributylbutoxysilane, phenyltrimethoxysilane, diphenyldiethoxysilane, and triphenylmethoxysilane;

(alkyl)alkoxysilanes having an isocyanato group such as 3-isocyanatopropyltrimethoxysilane, 3-isocyanatopropyltriethoxysilane, 2-isocyanato-ethyltriethoxysilane, 2-isocyanato-ethyltri-n-propoxysilane, 2-isocyanato-ethylethylidibutoxysilane, 3-isocyanatopropylmethylmethoxysilane, 3-isocyanatopropylethyldiethoxysilane, 3-isocyanatopropyldimethyl-iso-propoxysilane, 3-isocyanatopropyldiethylethoxysilane, 2-isocyanato-ethyldiethylbutoxysilane, di(3-isocyanatopropyl)diethoxysilane, di(3-isocyanatopropyl)methylethoxysilane, and ethoxytriisocyanatosilane;

(alkyl)alkoxysilanes having an epoxy group such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropylmethylmethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 3-glycidoxypropyldimethylethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and 3,4-epoxybutyltrimethoxysilane;

(alkyl)alkoxysilanes having a carboxyl group such as carboxymethyltriethoxysilane, carboxymethylethyldiethoxysilane, and carboxyethylmethyldimethoxysilane;

alkoxysilanes having an acid anhydride group such as 3-(triethoxysilyl)-2-methylpropylsuccinic anhydride;

alkoxysilanes having an acid halide group such as 2-(4-chlorosulfonylphenyl)ethyltriethoxysilane;

(alkyl)alkoxysilanes having an amino group such as 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropylmethylmethoxysilane, and N-phenyl-3-aminopropyltrimethoxysilane;

(alkyl)alkoxysilanes having a thiol group such as 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 2-mercaptoethyltriethoxysilane, and 3-mercaptopropylmethylmethoxysilane;

(alkyl)alkoxysilanes having a vinyl group such as vinyltrimethoxysilane, vinyltriethoxysilane, and vinylmethyldiethoxysilane;

(alkyl)alkoxysilanes having a methacryl group such as 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, and 3-methacryloxypropylmethylmethoxysilane;

(alkyl)alkoxysilanes having a halogen atom such as triethoxyfluorosilane, 3-chloropropyltrimethoxysilane, 3-bromopropyltriethoxysilane, and 2-chloroethylmethyldimethoxysilane; and

alkylalkoxysilanes employing an alkoxy group as a functional group such as isopropyltri-isopropoxysilane, and tri-isopropylisopropoxysilane.

[0039] Substantially the same compounds as described above except that the metal element other than silicon, for example Ti, Zr, Fe, Cu, Sn, B, Al, Ge, Ce, Ta, or W is used, are also included in the scope of metal alkoxide (B) of the present invention.

[0040] Specific examples of such compounds include monoisocyanatotrialkoxymetals such as 2-isocyanato-ethyltripropoxyzirconium, and 2-isocyanato-ethyltributoxytin;

monoisocyanatodialkoxymetals such as 3-isocyanatopropylmethyldi-isopropoxytitane, 2-isocyanato-ethylethylidipropoxyzirconium, 2-isocyanato-ethylmethyldibutoxytin, and isocyanatomethyldimethoxyaluminum;

monoisocyanatomonoalkoxymetals such as 3-isocyanatopropyldimethylisopropoxytitane, 2-isocyanato-ethyldiethylpropoxyzirconium, 2-isocyanato-ethyldimethylbutoxytin, and isocyanatomethylmethoxymethylmethoxyaluminum;

metal alkoxides employing an epoxy group as a functional group such as 3-glycidoxypropyltriisopropoxytitane, 3-glycidoxypropylmethyldi-isopropoxytitane, 3-glycidoxypropyldimethylisopropoxytitane, 3,4-epoxybutyltripropoxyzirconium, 3,4-epoxybutyldipropoxyzirconium, 3,4-epoxybutyldimethylpropoxysirconium, and β -(3,4-epoxycyclohexyl)ethyltriethoxytin.

[0041] Metal alkoxide (B) may be used alone or in combination of not less than two thereof. The metal alkoxide compound which includes not less than two kinds of metal such as $\text{Mg}[\text{Al}(\text{iso-OC}_3\text{H}_7)_4]_2$, $\text{Ba}[\text{Zr}_2(\text{OC}_2\text{H}_5)_9]_2$.

$(C_3H_7O)_2Zr[Al(OC_3H_7)_4]_2$, or the oligomer type metal alkoxide compound which includes not less than two repeating unites in the molecule such as tetramethoxysilane oligomer, tetraethoxysilane oligomer are also employed. The alkoxy group of metal alkoxide (B) may be an acetoxy group.

5 Polymer (C)

[0042] Polymer (C) of the present invention is the polymer which has at least one metal alkoxide group in the molecule and has a polycarbonate and/or a polyarylate moiety as a main frame. Polymer (A) and metal alkoxide (B) of the present invention are reacted by the conventional process optionally in the presence of catalyst to obtain polymer (C).

10 [0043] In case that a functional group of metal alkoxide (B) is an isocyanato group, or an acid halide group, and a functional group of polymer (A) is a hydroxyl group, an amino group, a carboxyl group, or a thiol group, an organic base compound such as 1,4-diazabicyclo[2,2,2]octane (DABCO), 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), triethylamine, tributylamine, piperidine, or the like is generally employed as the catalyst.

15 [0044] In case that a functional group of metal alkoxide (B) is an epoxy group, and a functional group of polymer (A) is a hydroxyl group, an amino group, a carboxyl group, or a thiol group, an acid compound such as hydrochloric acid, sulfuric acid, nitric acid, acetic acid, or the like is generally employed as the catalyst.

[0045] In case that a functional group of metal alkoxide (B) is a carboxyl group, an acid anhydride group, or an alkoxy group, and a functional group of polymer (A) is a hydroxyl group, an amino group, a carboxyl group, or a thiol group, both the base compound and the acid compound may be employed as the catalyst.

20 [0046] In case that a functional group of polymer (A) is an alkenyl group or an alkynyl group, polymer (A) and a silicone compound having a silane group (Si-H group) are subjected to the hydrosilylation reaction to obtain polymer (C) in which an alkoxyisilyl group is introduced.

[0047] Specific examples of the reaction process between metal alkoxide (B) and polymer (A) are described below.

25 [0048] In the first method, polymer (A) which has a functional group comprising an active hydrogen such as a hydroxyl group, an amino group, a carboxyl group, a thiol group or the like, is allowed to react with metal alkoxide (B) which has a functional group such as an isocyanato group, an epoxy group, a carboxyl group, an acid halide group, an acid anhydride group or the like, in a solvent, preferably under an inert gas atmosphere. The solvent employed may be those which can dissolve both polymer (A) and metal alkoxide (B).

30 [0049] The reaction is generally conducted by adding metal alkoxide (B) or a solution thereof to a solution of polymer (A), followed by stirring the resultant at room temperature or with slightly heating. It is preferable that the equivalent weight ratio of a functional group contained in metal alkoxide (B) based on polymer (A) is 1/10 to 10.

[0050] After the end of the reaction, the sol-gel reaction may subsequently be conducted by using the resulting reaction mixture. Otherwise, the reaction mixture is evaporated or poured into a less-soluble solvent to precipitate a reaction product, the reaction product is washed, purified, and dried, and then the sol-gel reaction is conducted by using the reaction product.

35 [0051] In the second method, polymer (A) which has a functional group comprising an active hydrogen is allowed to react with metal alkoxide (B) which is tetra-alkoxymetal or trialkoxymetal, in a solvent, preferably under an inert gas atmosphere. A functional group in polymer (A) preferably bonds to an aliphatic chain of polymer (A), and the carbon number of an alkoxide group in metal alkoxide (B) is preferably as small as possible, in order to conduct the reaction advantageously.

40 [0052] The solvent employed have to be those which can dissolve both polymer (A) and metal alkoxide (B). The reaction without water is preferred, and a non-polar solvent or a dehydrated solvent is preferably employed. It is preferable that the reaction is conducted in the presence of a catalyst in the catalytic amount. Examples of the catalyst include an acidic catalyst such as hydrochloric acid, sulfonic acid, and acetic acid; a basic catalyst such as triethylamine, DBU, and piperidine; and a metallic catalyst such as ferric chloride, ferrous chloride, and zinc chloride.

45 [0053] It is preferable that the equivalent weight ratio of a functional group contained in metal alkoxide (B) based on that of polymer (A) is 1/4 to 100.

[0054] After the end of the reaction, the sol-gel reaction may subsequently be conducted by using the resulting reaction mixture. Otherwise, the reaction mixture is evaporated or poured into a less-soluble solvent to precipitate a reaction product, the reaction product is washed, purified, and dried, and then the sol-gel reaction is conducted by using the reaction product.

[0055] In the third process, polymer (A) having a functional group such as an alkenyl group and an alkynyl group, and metal alkoxide (B) which is a silicone compound having a Si-H group are subjected to the hydrosilylation reaction.

50 [0056] The hydrosilylation reaction is preferred to be conducted in a solvent in the presence of a catalyst. Examples of the catalyst generally include a transition metal complex such as chloroplatinic acid, 1,3-divinyl-1,1,3,3-tetramethyl-disiloxaneplatinum complex, and tris(triphenylphosphine)rhodium chloride.

[0057] Examples of the solvent employed for the sol-gel reaction include a hydrocarbon solvent such as benzene, toluene, xylene, ethyl benzene, and n-hexane; a halogenated hydrocarbon solvent such as carbon tetrachloride, chloro-

form, dichloromethane, chloroethane, dichloroethane, chlorobenzene, dichlorobenzene, and trichlorobenzene; an ether solvent such as tetrahydrofuran, 1,4-dioxane, 1,3-dioxane, diethyl ether, and dibutyl ether; a ketone solvent such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, but is not limited to these examples.

5 [0058] A main frame of polymer (C) prepared as described above, may be composed of any one of polycarbonate, polyester carbonate, or polyarylate, or copolymer thereof. A main frame of polymer (C) may be composed of a mixture of the plural polymers, and it may be linear or branched. Polymer (C) is preferably soluble in a solvent such as hydrocarbon, halogenated hydrocarbon, and ether, and has a number average molecular weight of from 500 to 50000, more preferably 1000 to 15000.

10 [0059] A metal alkoxide group of polymer (C) has a central metal element selected from the group consisting of Si, Ti, Zr, Fe, Cu, Sn, B, Al, Ge, Ce, Ta, and W, preferably the group consisting of Si, Ti, and Zr; and 1 to 5 alkoxide group having 1 to 8, preferably 1 to 4 carbon atoms. Particularly preferred central metal element is Si because silicone alkoxide is easy to apply for general purpose.

[0060] The metal alkoxide group equivalent weight of polymer (C) is 1 to 100, preferably 1 to 50, more preferably 2 to 10. If the the metal alkoxide group equivalent weight of polymer (C) is less than 1, performance of the resulting material may become poor, and if more than 100, the resulting material may become breakable.

15 [0061] The plural metal alkoxide groups present in polymer (C) may be the same or different. The metal alkoxide groups may be those which include not less than two kinds of metal, or the oligomer type metal alkoxide group which includes not less than two repeating unites.

20 Organic-inorganic Hybrid Polymer Material (1)

[0062] In the first embodiment of the present invention, polymer (C) having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group is hydrolyzed and polycondensed by the sol-gel reaction. The polymer (C) may be dissolved in the reaction mixture right after preparation, or be isolated.

25 [0063] Throughout the specification, the hydrolysis and polycondensation by the sol-gel process means the reaction process in which a polymer having a metal alkoxide group reacts with water, the metal alkoxide group converts to a hydroxyl group, and the hydroxyl group is simultaneously polycondensed with an adjacent hydroxymetal group (e.g., -Si(OH)₃) or an adjacent alkoxy metal group by dehydration or dealcoholation to form three-dimensional crosslinkages composed of inorganic covalent bond.

30 [0064] The water may be added to the reaction process in the amount sufficient for converting all of the alkoxy group to the hydroxyl group. Otherwise, water present in the reaction mixture, or moisture of an atmosphere may be utilized. The reaction is preferably conducted at from room temperature to 100°C for 0.5 to 24 hours. An acidic catalyst such as hydrochloric acid, sulfonic acid, acetic acid, benzenesulfonic acid, and p-toluenesulfonic acid, or a basic catalyst such as sodium hydroxide, potassium hydroxide, ammonia, triethylamine, piperidine, and DBU, may also be employed.

35 [0065] After the end of the reaction, the resulting material may further be heated at 50 to 400°C, for 5 minutes to 48 hours in order to surely proceed the polycondensation reaction and to form hard crosslinkages.

[0066] The metal selected from the group consisting of Si, Ti, Zr, Fe, Cu, Sn, B, Al, Ge, Ce, Ta, and W, and a metal compound thereof such as metal oxide, metal complex, metal salt, and the like may further be employed in the hydrolysis and polycondensation reaction of the present invention, in view of further improving strength, hardness, weather resistance, chemical resistance, flame resistance, static resistance of the resulting material; for newly supplying the performance to the material; or for controlling the inorganic content or the crosslinking density of the material.

40 [0067] An anti-drying agent such as formamide, dimethylformamide, dioxane, oxalic acid, or the other additives such as acetyl acetone, and the like may be included in the reaction mixture for the hydrolysis and polycondensation reaction of the present invention for preventing from forming the crack during the drying process.

45 Organic-inorganic Hybrid Polymer Material (2)

[0068] In the second embodiment of the present invention, polymer (C) having a polycarbonate and/or a polyarylate moiety as a main frame and having a metal alkoxide group as a functional group, and metal alkoxide (B) are cohydrolyzed and copolycondensed by the sol-gel reaction.

50 [0069] The ratio of the polymer (C) and metal alkoxide (B) may optionally be varied. The weight ratio of the polymer (C) and metal alkoxide (B) is generally 10:90 to 90:10.

[0070] The hydrolysis and polycondensation of the second embodiment of the present invention may be conducted by the procedure in which polymer (C) and metal alkoxide (B) are mixed and dissolved in a solvent beforehand, and then the resulting mixture is subjected to the sol-gel reaction, or that in which either polymer (C) or metal alkoxide (B) is hydrolyzed beforehand, then another is added, and the resulting mixture is subjected to the sol-gel reaction.

55 [0071] The organic-inorganic hybrid polymer material prepared by the procedure has the structure in which the two components are dispersed and bonded finely and uniformly, improving its heat resistance and mechanical strength.